INTEGRATION OF BIOTECHNOLOGY AND CATALYSIS FOR THE VALORIZATION OF WASTE STREAMS

Tomorrow's biorefineries in Europe

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Partners and expertise

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Biotechnologies

ARKEMA

C I R C C

Consorzio Interuniversitario REATTIVITA' CHIMICA E CATALISI

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Chemical technologies

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Biotechnologies

$$\begin{array}{l} CH_2-O-CO-R \\ | \\ CH-O-CO-R \\ | \\ CH_2-O-CO-R \end{array} + 3\ CH_3OH \xrightleftharpoons{\text{cat.}} \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + 3\ R-COOCH_3$$

TG **FAMEs** **glycerol (water and salts!)**

$$MOH + CH_3OH \longrightarrow CH_3O^-M^+ + H_2O$$

Watery

$$R-COOH + MOH \longrightarrow R-COO^-M^+ + H_2O$$

FFAs **soaps** M = Na, K

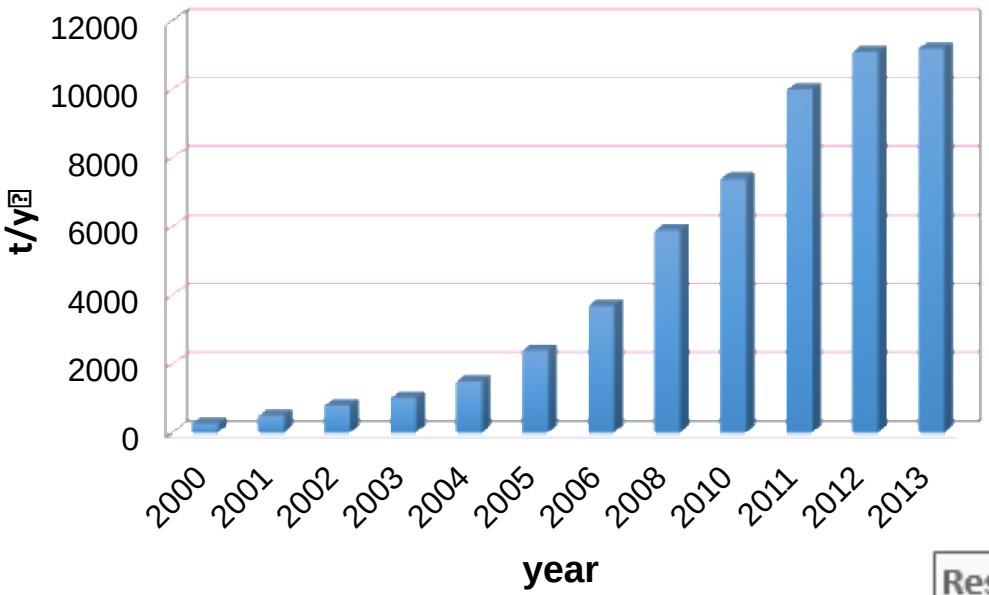
Water free

$$\begin{array}{l} CH_2-O-CO-R \\ | \\ CH-O-CO-R \\ | \\ CH_2-O-CO-R \end{array} + R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[\text{MeOH}]{\text{New catalyst}} R-COOCH_3$$

TG **FFAs 20+%** **FAMEs + glycerol**

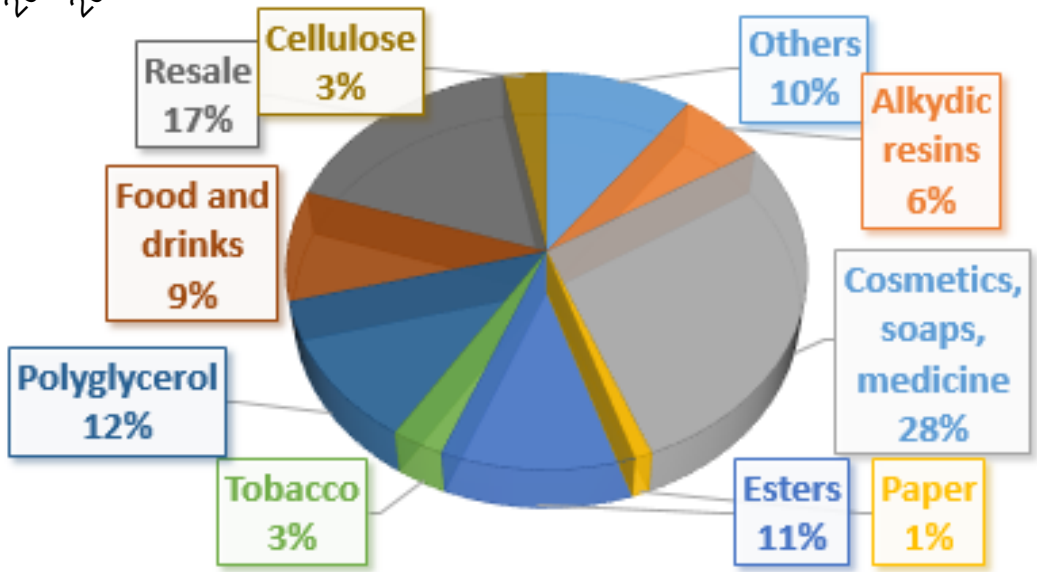
M. Aresta, A. Dibenedetto, A. Angelini, C. Pastore, L. di Bitonto, "New catalysts for the production of biodiesel from bio-oils", *Patent MI2013A001730*, 2013

EU market of bioglycerol and uses

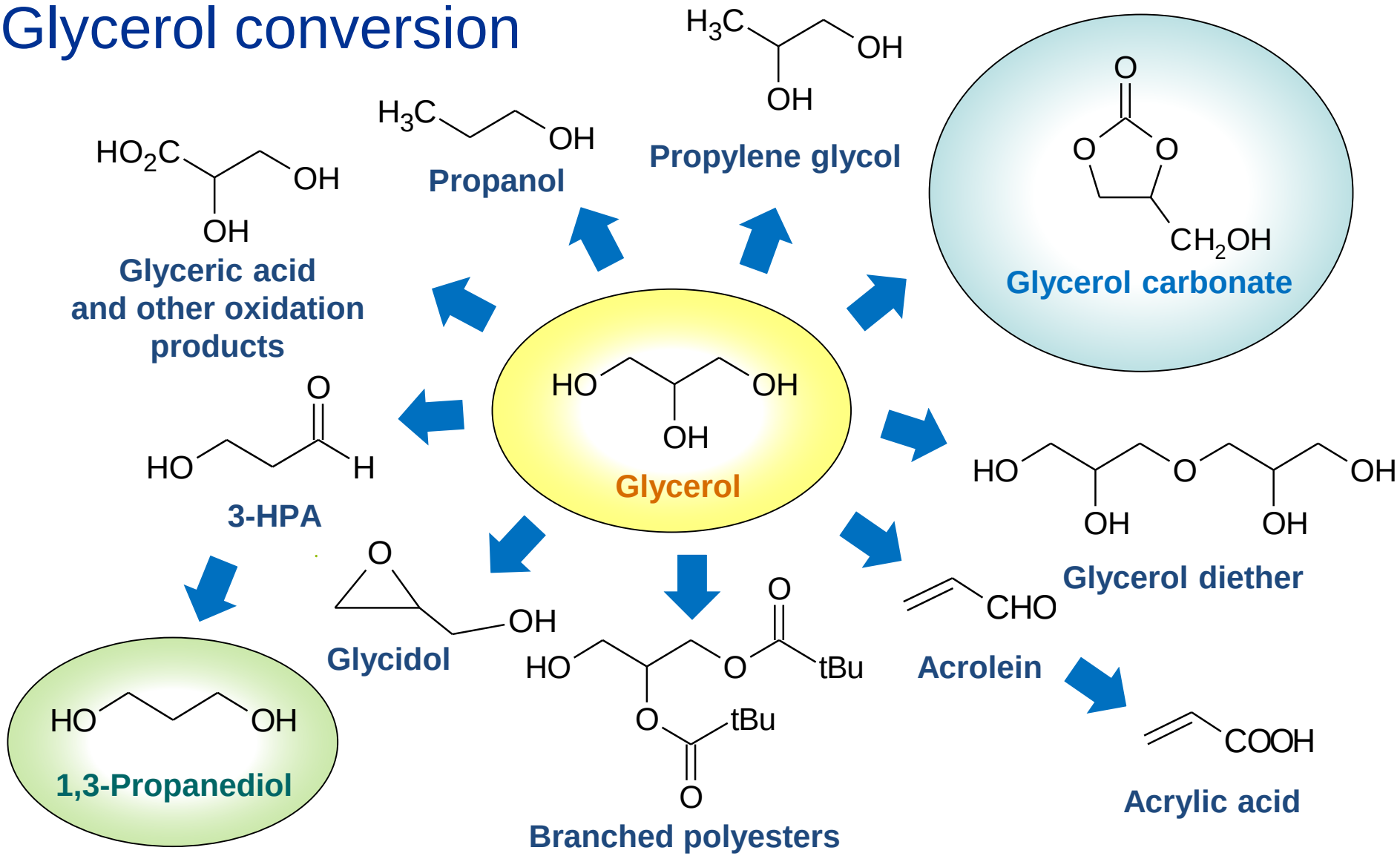


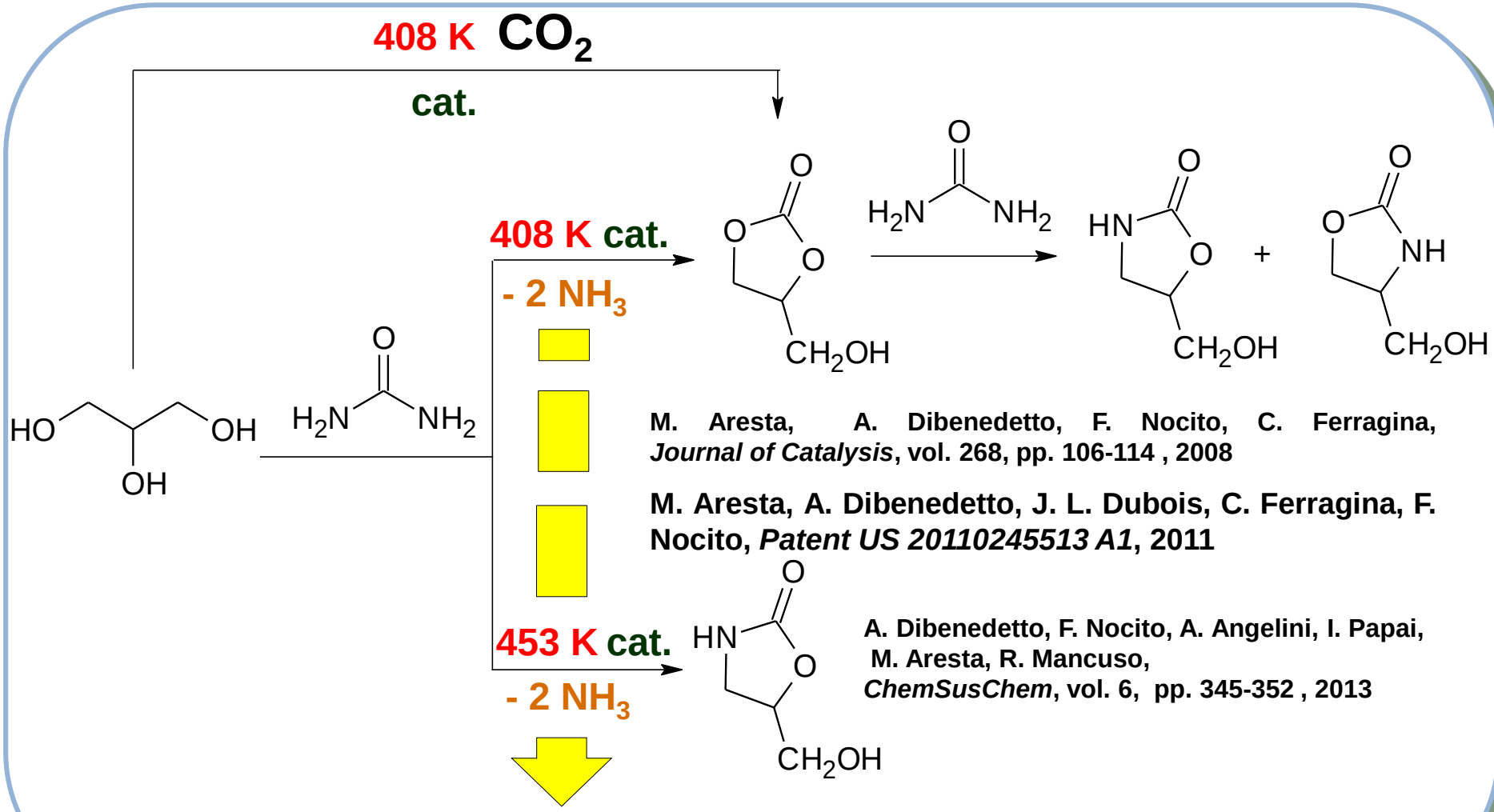
EU production of bioglycerol.

Main industrial applications of glycerol.



Glycerol conversion





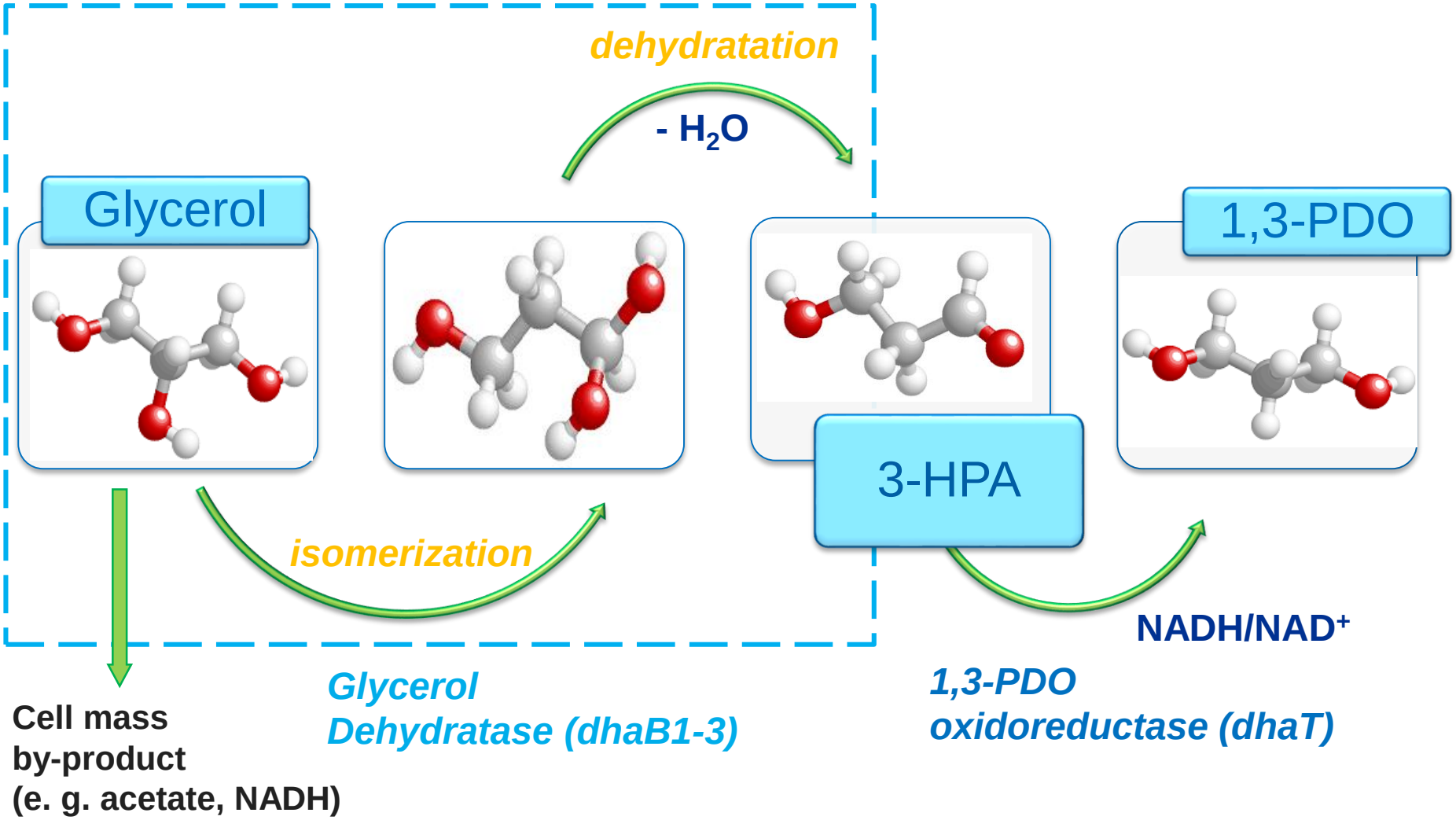
M. Aresta, A. Dibenedetto, F. Nocito, C. Ferragina, *Journal of Catalysis*, vol. 268, pp. 106-114 , 2008

M. Aresta, A. Dibenedetto, J. L. Dubois, C. Ferragina, F. Nocito, *Patent US 20110245513 A1*, 2011

A. Dibenedetto, F. Nocito, A. Angelini, I. Papai, M. Aresta, R. Mancuso, *ChemSusChem*, vol. 6, pp. 345-352 , 2013

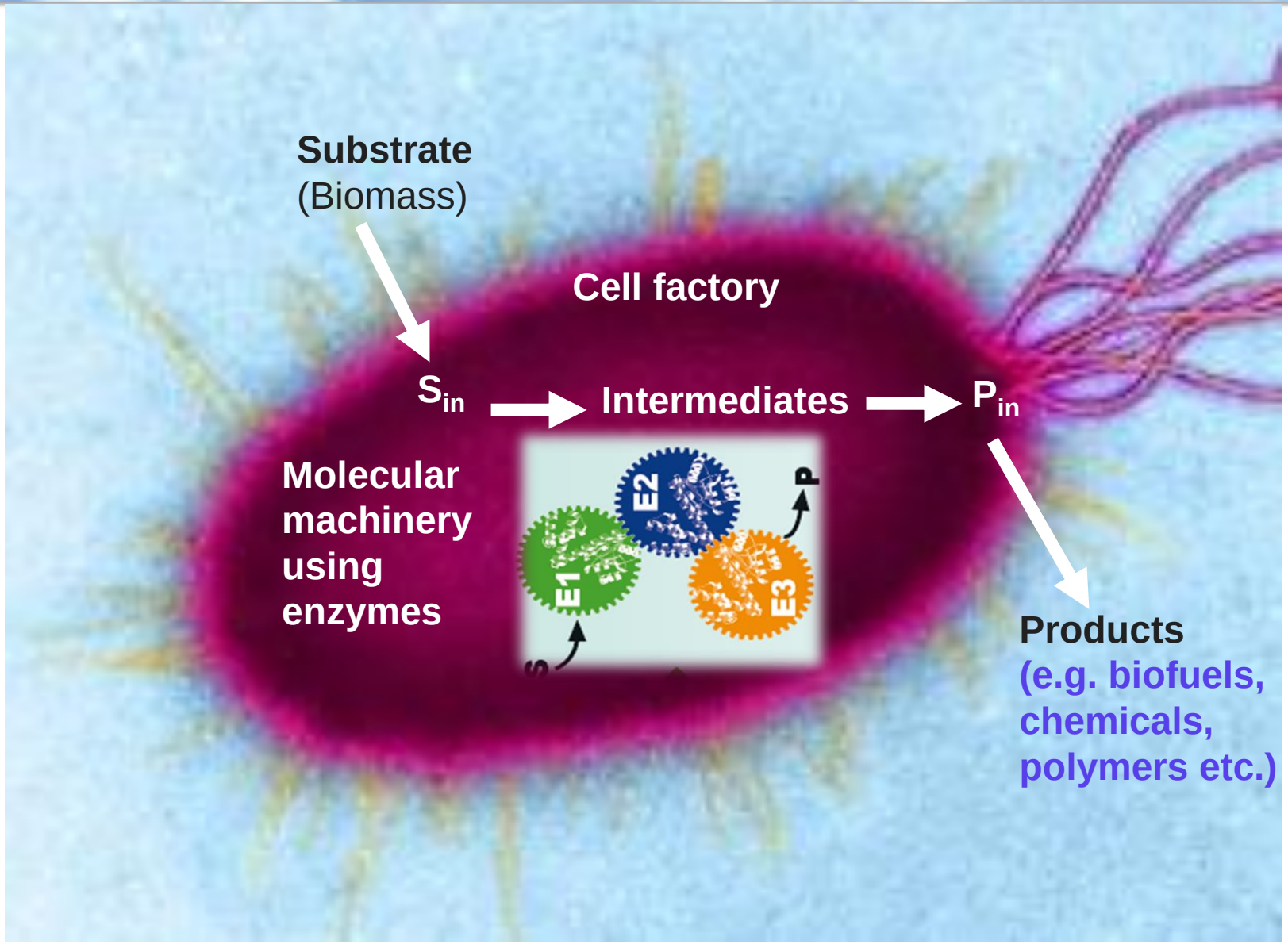
Synthesis of chemicals

Conversion of glycerol into 1,3-PDO



MICROBIAL

BIOCONVERSION

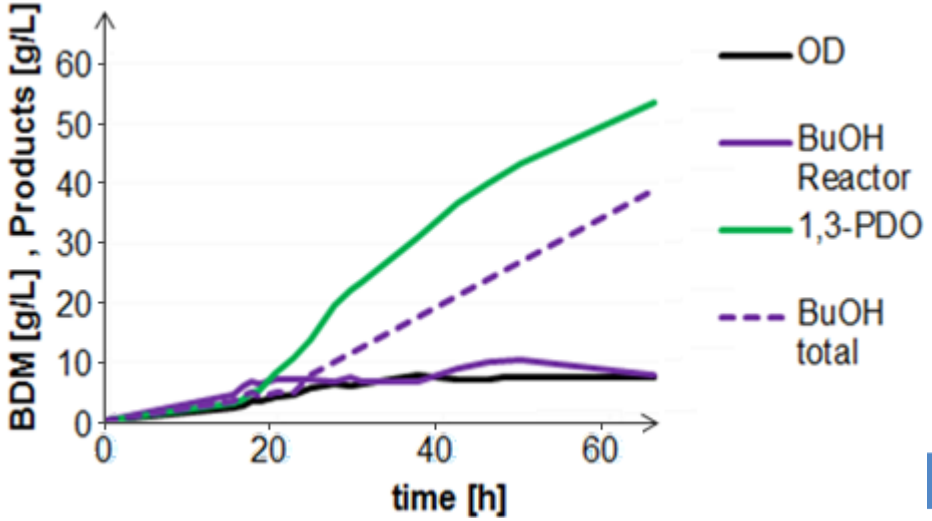


Bioproduction of 1,3-propanediol, n-butanol and biogas from raw glycerol and biomass hydrolysates

Laboratory

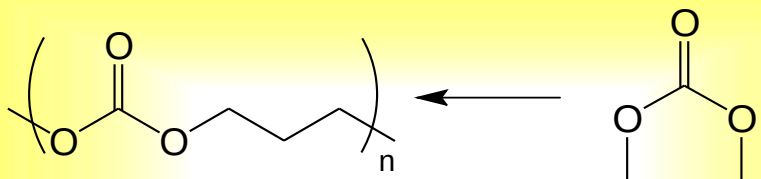
Miniplant process integration

Scale-up and demonstration



An adapted strain for simultaneous use of raw glycerol and hydrolysates.
Co-production of PDO and butanol.
In situ removal of butanol to reduce product inhibition

Conversion of 1,3-PDO into TMC



pTMC

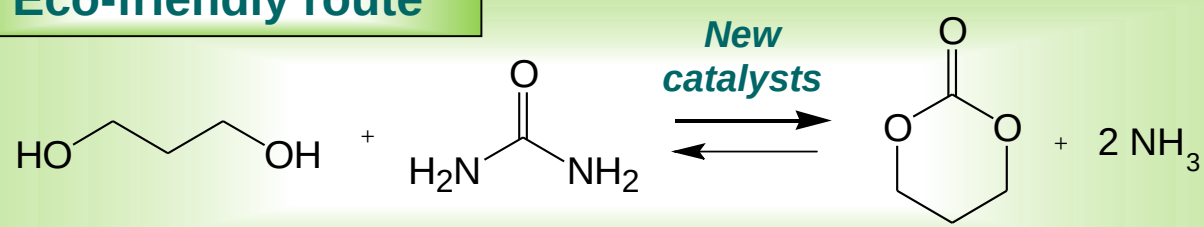
Also co-polymer with ε-caprolactone

TMC

Applications

- Biodegradable materials
- Polymers
- Film and coating materials

Eco-friendly route



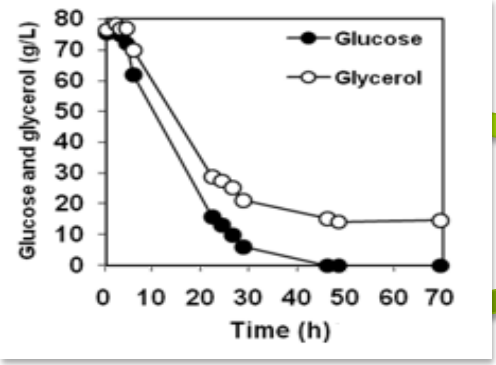
Utilization

Benefits

- Absence of reaction solvent
- Low costs of the reagents
- Catalysts recovery and recycle

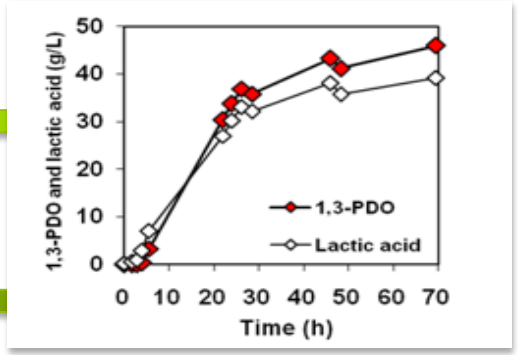
M. Aresta, A. Dibenedetto, L. di Bitonto, J. L. Dubois, "Synthesis process of Trimethylene carbonate from 1,3-propanediol and urea by heterogeneous catalysts",
***Patent EP 13192912.7*, 2013**

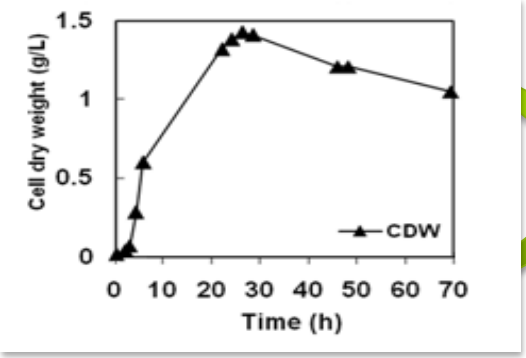
Conversion of glycerol into PDO using *Lactobacillus reuteri* DSM 20016



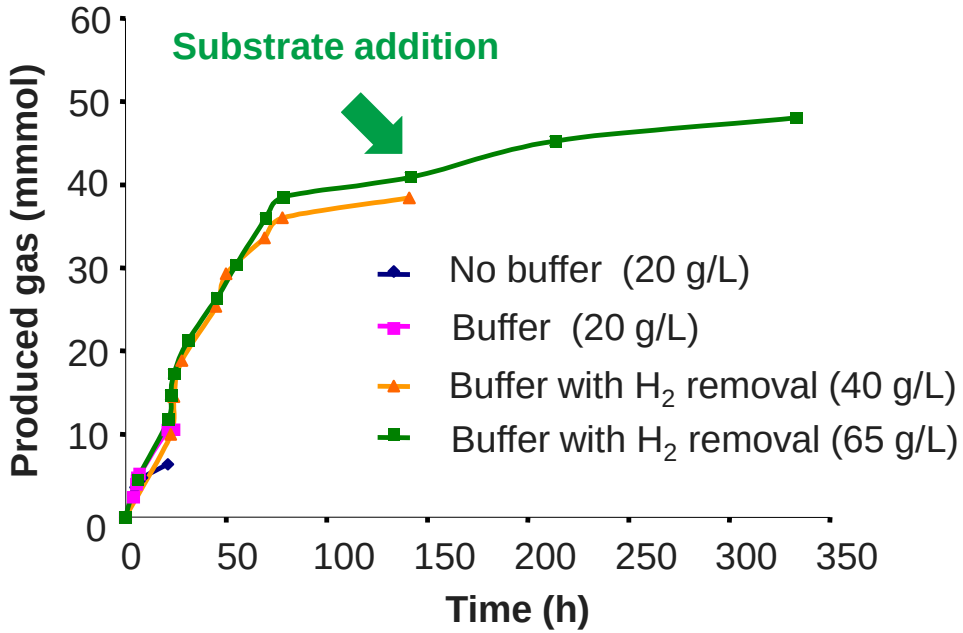
Glycerol-glucose co-fermentation

- ✓46 g/L of PDO obtained (33 g/L using raw glycerol)
- ✓Yield of 0.9 mol1,3-PDO/mol glycerol
- ✓*L. reuteri* DSM 20016 is a valuable probiotic. Biomass can be used.
- ✓Possibile to use raw glycerol and cellulosic hydrolisates as substrates





Hydrogen production from raw bioglycerol using **strain ADK1:** utilization for the **hydrogenation of polyenes**



Test conditions (g/L)	% Substrate consumption	% gas produced*	H_2 (not optimized, mmol/L·h)	P_{max} (atm)
No buffer (20)	88	58	14.28	3.2
Buffer (20)	**100**	**100**	**25.87**	**5.3**
Buffer with H_2 removal (40)	74	44	13.4	3.2
Buffer with H_2 removal (65)	64	34	14.38	3.6

* Respect to initial substrate 1:1 ratio

Chemical (VPR) *vs* biotechnological H_2 production from bioglycerol

Comparison of the biological* *vs* catalytic# production di dihydrogen from glycerol

Concentration of glycerol	**2-6 %***	**1 – 20 %#**
Conversion of glycerol	**100% at 2% feed**	**100% at 1% feed**
Purity of H_2	**> 99%**	**90%**
Presence of CO	**absent**	**yes**
Presence of CO_2	**traces**	**present**
Temperature	**ambient**	**500–600 K**
Pressure	**0.6 MPa**	**2.0–3.0 MPa**
Lifetime of the catalyst	**more than seven days**	**one week**
Co-products	**organic acids, ethanol: only traces**	**organic acids and others**

CONCLUSIONS

- **Integration of biotechnology and catalysis may bring to the valorization of waste streams, solid-liquid-gases**

- **The integration can be: “a sequence of operations” for the production/conversion of products, or “integrated technologies” for single product conversion**

- **This zero-waste approach, with recovery/reuse of co-products (ammonia) and use of recoverable and reusable heterogeneous catalysts, converts waste (liquid, solid, gases) into added value products**

- **This concept can find wide implementation**

Acknowledgements

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